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REFERENCE MATERIALS CZN-1, CPB-1, CCU-1, MP-1a AND MP-2: ADDITIONAL RECOMMENDED VALUES

H.F. STEGER AND W.S. BOWMAN

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REFERENCE MATERIALS CZN-1, CPB-1, CCU-1, MP-1a and MP-2: ADDITIONAL RECOMMENDED VALUES

by

Henry P. Steger* and W.S. Bowman**

SYNOPSIS

A second interlaboratory analytical program has been performed for reference materials CZN-1, CPB-1, CCU-1, MP-1a and MP-2 in order to assign recommended values for several elements which had not been sufficiently well characterized in the initial interlaboratory programs of 1978 to 1982. Ten laboratories under CANMET contract provided analytical results by methods of their choice. Based on a statistical analysis of the combined results of the present and initial programs, the following recommended values were assigned:

CZN-1: Bi, 27 µg/g; Sn, 65 µg/g; Se, 5.5 µg/g
CPB-1: Mn, 0.039%; Sn, 0.019%; Se, 30 µg/g
CCU-1: Fe, 30.87%; S, 35.4%; As, 41 µg/g; Se, 120 µg/g
MP-1 : W, 0.040%
MP-2 : Sn, 0.043%.

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MATÉRIAUX DE RÉFÉRENCE CZN-1, CPB-1, CCU-1, MP-1a et MP-2: VALEURS RECOMMANDÉES ADDITIONNELLES

par

Henry F. Steger* et W.S. Bowman**

RÉSUMÉ

Une deuxième campagne analytique interlaboratoires a été élaborée afin d'assigner des valeurs recommandées à plusieurs éléments des matériaux de référence CZN-1, CPB-1, CCU-1, MP-1a et MP-2 dont la caractérisation était incomplète au terme de la campagne initiale de 1978 à 1982. Dix laboratoires ont obtenu des contrats de CANMET pour produire des résultats analytiques à l'aide de méthodes de leur choix. L'analyse statistique des résultats combinés de la campagne actuelle et de la campagne initiale a permis d'assigner les valeurs suivantes:

CZN-1: Bi, 27 µg/g; Sn, 65 µg/g; Se, 5,5 µg/g
CPB-1: Mn, 0,039 %; Sn, 0,019 %; Se, 30 µg/g
CCU-1: Fe, 30,87 %; S, 35,4 %; As, 41 µg/g; Se, 120 µg/g
MP-1 : W, 0,040 %
MP-2 : Sn, 0,043 %.

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INTRODUCTION

The Canadian Certified Reference Materials Project (CCRMP) endeavors to provide compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. These reference materials are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

From time to time, it occurs that one or more of the elements or constituents of concern in a particular reference material are not sufficiently well characterized by an interlaboratory analysis program to permit CCRMP to assign a recommended value for its (or their) content in that material. Only additional analytical results or another interlaboratory program can overcome this shortcoming. This report summarizes the results of a second interlaboratory program performed in 1983/84 for CZN-1 (2), CPB-1 (3), CCU-1 (4), MP-1a (5) and MP-2 (6) and of their combination with the results of the initial interlaboratory programs. This permits the assignment of recommended values for bismuth, tin and selenium in CZN-1; manganese, tin and selenium in CPB-1; iron, sulphur, arsenic and selenium in CCU-1; tungsten in MP-1a; and tin in MP-2.

NATURE AND PREPARATION

The origin, physical preparation, chemical and mineralogical compositions and particle size distributions have been reported previously for CZN-1 (2), CPB-1 (3), CCU-1 (4), MP-1a (5) and MP-2 (6).

INTERLABORATORY PROGRAM

Laboratories participating under CANMET contract in the interlaboratory program of 1983/84 are listed by laboratory number in Appendix A. They were requested to contribute five replicate results for the elements of interest on one bottle of the reference material by a method of their choice and to report the results on an 'as is' basis. Where a laboratory reported two sets of results for an element, these sets were deemed to be statistically independent. The recommended values are given in Table 1. Methodological information for the present interlaboratory program is reported in Table 2. All available analytical information is summarized in Table 3; data from the present interlaboratory program are reported with the corresponding laboratory number.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing the statistics. All results that were rejected are identified in Table 3.

ESTIMATION OF CONSENSUS VALUES AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (7).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,

μ = the true consensus value,

y_i = the discrepancy between the mean of the results in the set i ($\bar{x}_i$.) and μ, and

e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i$.

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and the appropriate degrees of freedom.

Table 1 - Recommended values and statistical parameters (outliers excluded)

Reference material	Element	No. of laboratories	No. of results	Overall mean	95% CL Low	95% CL High	σ_A
CZN-1	Bi	17	148	27 µg/g	24	30	2
	Sn	14	103	65 µg/g	52	77	5
	Se	14	113	5.5 µg/g	4.5	6.6	0.6
CPB-1	Mn	22	187	0.039%	0.037	0.040	0.001
	Sn	13	93	0.019%	0.014	0.024	0.001
	Se	15	106	30 µg/g	27	32	1
CCU-1	Fe	10	70	30.87%	30.64	31.10	0.08
	S	13	90	35.4%	34.9	35.9	0.2
	As	20	156	41 µg/g	38	45	3
	Se	15	113	120 µg/g	111	129	5
MP-1a	W	20	100	0.040%	0.035	0.044	0.002
MP-2	Sn	12	65	0.043%	0.040	0.045	0.002

The consensus value of the assumed model is estimated by $\bar{\bar{x}}..$ the mean of the mean of each set:

$$\bar{\bar{x}}.. = \sum_{i}^{k} \bar{x}. \Big/ k$$

where k = the number of sets.

The overall mean was calculated using individual laboratory mean values rather than individual values as is the usual practice in CCRMP because of the inequality in the number of replicate results from each laboratory provided in the initial and current interlaboratory programs for CZN-1, CPB-1 and CCU-1. Replication was ten and five, respectively, which would give the laboratories of the initial program twice the weighting of those of the current program in the calculation of overall mean values using individual results.

The value of σ^2 is esimated by s_1^2 which is given by

$$s_1^2 = \sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_{i}^{k} n_i - k.$$

where n_i = the number of results set in i.

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1} \left(\sum_{i}^{k} n_i - \sum_{i}^{k} n_i^2 \Big/ \sum_{i}^{k} n_i \right)$$

where

$$s_2^2 = \sum_{i}^{k} n_i (\bar{x}_i. - \bar{\bar{x}}..)^2 \Big/ k-1.$$

The variance of the overall mean is given by

$$V[\bar{\bar{x}}..] = \left(\sum_{i}^{k} n_i^2 / (\sum_{i}^{k} n_i)^2 \right) \omega^2 + \left(1/\sum_{i}^{k} n_i \right) \sigma^2$$

and the 95% confidence limits for $\bar{\bar{x}}..$ are

$$\bar{\bar{x}}.. \pm t_{0.975,\,(k-1)} \sqrt{V[\bar{\bar{x}}..]}$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 cases would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

Table 2a - Methodological information for CZN-1 and CPB-1

Element	Reference material	Laboratory number	Finish	Separation, decomposition, etc.
Bi	CZN-1	2,3,7,9	Atomic absorption	Mixed acid decomposition
		6,8	Atomic absorption (flameless)	Mixed acid decomposition; BiH_4 generation; quartz tube
		5	Atomic absorption	Mixed acid decomposition; Bi extracted with cupferron in MIBK. Organic destroyed and taken up in HCl
		4	No details	
Sn	CZN-1, CPB-1	2,3,5	Atomic absorption	Na_2O_2 + Na_2CO_3 fusion; taken up in dilute HCl
		6	Atomic absorption (flameless)	Na_2O_2 + Na_2CO_3 fusion; SnH_4 generation
		8	"	Mixed acid decomposition; SnH_4 generation
		7	Xrf	
		4	No details	
Se	CZN-1, CPB-1	3	Atomic absorption (flameless)	Mixed acid decomposition, H_2Se generation
		6	"	Mixed acid decomposition; Se extracted with 2,3-diaminonaphthlene; H_2Se generation
		10	"	$K_2S_2O_7$ fusion; H_2Se generation
		7,9	Colorimetry	Mixed acid decomposition; colour formation with diaminobenzidine
		8	ICP-AE	Mixed acid decomposition
		4	No details	
	CZN-1	1	INAA	Instrumental Neutron Activation Analysis
	CPB-1	2	Colorimetry	Mixed acid decomposition; colour formation with diaminobenzidine
Mn	CPB-1	2,3,4,5,6, 7,8,9,10	Atomic absorption	Mixed acid decomposition
		1	INAA	Instrumental Neutron Activation Analysis

Table 2b - Methodological information for CCU-1

Element	Laboratory number	Finish	Separation, decomposition, etc.
Fe	7,8,10	Atomic absorption	Mixed acid decomposition
	3,4,5,9	Titrimetry	Mixed acid decomposition; dichromate titration
	2	"	Na_2O_2 + Na_2CO_3 fusion; Fe_2O_3 precipitation with NH_4OH; dichromate titration
	1	INAA	Instrumental Neutron Activation Analysis
	6	Xrf	$K_2S_2O_7$ fusion; ground and pelletized
S	3,6,8	Gravimetry	Mixed acid decomposition; S precipitated as $BaSO_4$
	5,6,7	"	HNO_3 + HCl + BR_2; S precipitated as $BaSO_4$
	5a	"	K_2CO_3 + KNO_3 fusion; carbonates filtered off; S precipitated as $BaSO_4$
	2,9,10	Titrimetry	Leco Induction Furnace combustion; iodimetric titration
	1	PRGAMA	Prompt Gamma Acitivation Analysis
	4	No details	
As	8,10b	Atomic absorption (flameless)	Mixed acid decomposition; arsine generation
	10a	"	$K_2S_2O_7$ fusion; arsine generation
	2,3,5,7,9	Colorimetry	Mixed acid decomposition; arsine generated and trapped in silver diethyldithiocarbonate in pyridine
	1,6	INAA	Instrumental Neutron Activation Analysis
	4	No details	
Se	3	Atomic absorption (flameless)	Mixed decomposition; H_2Se generation
	6	Atomic absorption (graphite furnace)	Mixed acid decomposition; Se(IV) extracted with 2,3-diamino-naphthalene
	2,7,9	Colorimetry	Mixed acid decomposition; colour formation with diaminobenzidine
	8	Xrf	
	4	No details	

Table 2c - Methodological information for tungsten in MP-1a

Laboratory number	Finish	Decomposition, separation, etc.
1,6	INAA	Instrumental Neutron Activation Analysis
3,5,10	Colorimetry	$K_2S_2O_7$ fusion; colour development with KSCN
2,7,8	Xrf	Briquette
4	No details	

Table 2d - Methodological information for tin in MP-2

Laboratory number	Finish	Decomposition, separation, etc.
3,5	Atomic absorption	Na_2O_2 + Na_2CO_3 fusion; R_2O_3 separation; taken up in dilute HCl
8	Atomic absorption (flameless)	Mixed acid decomposition; tin hydride generation
2,7	Xrf	Briquette
6	Xrf	Silica sand + binder briquette

Table 3a - Analytical results, laboratory means and standard deviations for bismuth in CZN-1

Table 3a - Analytical results, laboratory means and standard deviations for bismuth in CZN-1

BISMUTH UG/G

							MEAN	S.D.
	(AA)	89.3000	106.3000	95.2000	83.3000	83.3000	92.3200	9.6434
		89.3000	100.0000	93.8000	105.3000	77.4000		
	(COLOR)	23.0000	22.4000	21.2000	21.4000	22.5000	22.7500	.9490
		23.6000	24.4000	23.0000	23.0000	23.0000		
	(AA)	25.0000	25.0000	25.0000	27.0000	25.0000	25.4000	.8433
		25.0000	27.0000	25.0000	25.0000	25.0000		
	(AA)	100.0000	110.0000	110.0000	120.0000	140.0000	122.000013.1656	
		130.0000	140.0000	120.0000	120.0000	130.0000		
	(AA)	56.0000	58.0000	58.0000	60.0000	56.0000	57.7000	2.0028
		61.0000	56.0000	60.0000	58.0000	56.0000		
	(AA)	601.2020	601.2020	601.2020	601.2020	601.2020	601.2020	.0000
		601.2020	601.2020	601.2020	601.2020	601.2020		
	(AA)	23.0000	17.0000	15.0000	23.0000	18.0000	19.3333	3.2660
		20.0000						
	(AA)	24.0000	27.0000	27.0000	27.0000	25.0000	26.1000	1.2202
		27.0000	27.0000	27.0000	25.0000	24.0000		
	(AA)	70.0000	70.0000	70.0000	60.0000	70.0000	70.0000	4.7140
		80.0000	70.0000	70.0000	70.0000	70.0000		
	(AA)	32.0000	29.0000	32.0000	25.0000	32.0000	29.7500	2.8447
		30.0000	29.0000	27.0000	37.0000	30.0000		
		30.0000	32.0000	30.0000	25.0000	30.0000		
		27.0000	29.0000	33.0000	27.0000	29.0000		
	(COLOR)	30.0000	36.0000	37.0000	49.0000	27.0000	32.2000	7.1616
		25.0000	31.0000	25.0000	30.0000	32.0000		
	(AA)	25.0000	25.0000	25.0000	25.0000	25.0000	25.0000	0.0000
		25.0000	25.0000	25.0000	25.0000	25.0000		
	(AA)	23.7000	23.2000	23.8000	23.7000	24.0000	23.5200	.4211
		23.5000	22.7000	23.7000	23.0000	23.9000		
	(AA)	36.0000	30.0000	28.0000	44.0000	36.0000	34.2500	6.7974
		34.0000	36.0000	35.0000	22.0000	44.0000		
		40.0000	26.0000					
	(AA)	22.0000	23.2000	22.8000	21.6000	24.0000	23.0000	1.2915
		24.0000	24.4000	21.6000	22.4000	22.0000		
	(ES)	30.0000	35.0000	28.0000	25.0000	20.0000	27.6000	5.5946
	(ES)	20.0000	15.0000	20.0000	20.0000	25.0000	19.0000	3.1623
		20.0000	20.0000	20.0000	15.0000	15.0000		
LAB- 2	(AA)	37.7	37.7	38.3	37.7	37.9	37.8600	.2608
LAB- 3	(AA)	57.	62.	59.	59.	59.	59.2000	1.7889
LAB- 4	(AA)	80.	70.	80.	70.	70.	78.0000	7.0711
LAB- 5	(AA)	30.	25.	27.	29.	27.	27.6000	1.9494
LAB- 6	(AA)	30.	28.	29.	27.	27.	28.2000	1.3038
LAB- 7	(AA)	95.	88.	94.	96.	91.	92.0000	3.2711
LAB- 8	(AA)	26.39	26.35	25.68	26.34	25.39	26.0220	.4777
LAB- 9	(AA)	35.	40.	39.	39.	35.	37.4000	2.3022

Table 3b - Analytical results, laboratory means and standard deviations for tin in CZN-1

TIN UG/G

							MEAN	S.D.
	(COLOR)	75.0000	75.0000	76.0000	76.0000	74.0000	77.5000	4.4535
		76.0000	76.0000	89.0000	77.0000	81.0000		
	(ES)*	200.0000	260.0000	220.0000	200.0000	240.0000	209.0000	24.2441
		200.0000	190.0000	200.0000	180.0000	200.0000		
	(POLAR)	72.0000	70.0000	80.0000	72.0000	72.0000	72.0000	3.0185
		69.0000	72.0000	72.0000	71.0000	70.0000		
	(ES)	20.0000	20.0000	20.0000	20.0000		20.0000	0.0000
	(AA)	100.0000	80.0000	80.0000	80.0000	80.0000	90.5000	13.5627
		100.0000	100.0000	80.0000	100.0000	100.0000		
		80.0000	50.0000	100.0000	100.0000	100.0000		
		100.0000	100.0000	100.0000	100.0000	80.0000		
	(COLOR)	48.9000	52.9000	47.5000	50.9000	48.9000	49.7100	1.7110
		50.4000	50.8000	48.5000	47.6000	50.7000		
	(ES)	105.0000	80.0000	110.0000	85.0000	90.0000	94.0000	12.9422
	(ES)	85.0000	75.0000	68.0000	64.0000	67.0000	70.9000	7.0624
		72.0000	80.0000	67.0000	67.0000	64.0000		
LAB- 2	(AA)	76.	78.	75.	76.	75.	76.0000	1.2247
LAB- 3	(AA)	71.	71.	71.	71.	71.	71.0000	0.0000
LAB- 4	(XRF)	55.	58.	47.	50.	51.	52.2000	4.3243
LAB- 5	(AA)	70.	70.	78.	60.	62.	68.0000	7.2111
LAB- 6	(AA)	65.	68.	65.	63.	68.	65.8000	2.1679
LAB- 7	(XRF)	38.	42.	40.	35.	36.	38.2000	2.8636
LAB- 8	(AA)	64.	60.	68.	60.	68.	64.0000	4.0000

*Outlying set.

Table 3c - Analytical results, laboratory means and standard deviations for selenium in CZN-1

SELENIUM UG/G

							MEAN	S.D.
	(COLOR)	8.0000	7.7000	7.0000	7.7000	7.7000	6.7100	1.0290
		6.2000	5.7000	5.7000	5.2000	6.2000		
	(COLOR)	5.0000	5.6000	4.8000	4.6000	4.6000	4.9600	.2951
		5.0000	4.8000	5.0000	5.2000	5.0000		
	(COLOR)	3.6000	4.4000	4.8000	4.4000	4.2000	4.4400	.3502
		4.6000	4.4000	4.8000	4.6000	4.6000		
	(COLOR)	3.9000	4.0000	4.2000	4.0000	3.9000	3.9900	.2079
		4.4000	3.9000	3.6000	4.0000	4.0000		
	(AA)	5.0100	5.0100	5.0100	5.0100	6.0120	5.3110	.5281
		6.0120	5.0100	6.0120	6.0120	6.0120		
	(AA)	3.2000	5.8000	6.1000	5.2000	4.8000	5.3500	1.0784
		4.9000	6.3000	6.5000				
	(COLOR)	6.0000	6.0000	6.0000	6.0000	6.0000	6.0000	0.0000
		6.0000	6.0000	6.0000	6.0000	6.0000		
	(AA)	4.7000	5.2000	5.4000	4.9000	5.3000	5.0100	.3604
		4.7000	5.1000	5.6000	4.6000	4.6000		
	(AA)	3.3000	3.4000	3.5000	3.3000	3.5000	3.1700	.2791
		2.7000	2.9000	3.0000	2.9000	3.2000		
LAB- 4	(COLOR)	2.	4.	4.	4.	2.	3.2000	1.0954
LAB- 6	(AA)	5.4	5.4	5.5	5.4	5.4	5.4200	.0447
LAB- 7	(COLOR)	8.	9.	9.	10.	8.	8.8000	.8367
LAB- 8	(ICP)	10.	12.	10.	10.	10.	10.4000	.8944
LAB- 9	(COLOR)*	84.	73.	80.	78.	80.	79.0000	4.0000
LAB-10	(AA)	4.6	4.6	4.2	4.2	4.2	4.3600	.2191

*Outlying set.

Table 3d - Analytical results, laboratory means and standard deviations for manganese in CPB-1

MANGANESE WT %

							MEAN	S.D.
	(COLOR)	.0392	.0402	.0400	.0392	.0395	.0395	.0004
		.0392	.0395	.0392	.0392	.0395		
	(AA)	.0360	.0360	.0360	.0370	.0370	.0365	.0007
		.0350	.0370	.0370	.0370	.0370		
	(AA)	.0400	.0420	.0420	.0420	.0400	.0408	.0010
		.0400	.0400	.0400	.0420	.0400		
	(AA)	.0390	.0400	.0410	.0390	.0400	.0403	.0008
		.0410	.0410	.0410	.0400	.0410		
	(AA)	.0380	.0380	.0370	.0370	.0370	.0373	.0005
		.0370	.0370	.0370	.0370	.0380		
	(AA)	.0420	.0420	.0420	.0420	.0420	.0420	.0000
		.0420	.0420	.0420				
	(AA)	.0375	.0365	.0365	.0370	.0365	.0371	.0005
		.0370	.0370	.0380	.0375	.0370		
	(AA)	.0430	.0440	.0430	.0430	.0430	.0431	.0006
		.0440	.0430	.0430	.0430	.0420		
	(AA)	.0420	.0420	.0390	.0420	.0400	.0406	.0010
		.0400	.0400	.0400	.0400	.0400		
		.0420	.0400	.0400	.0400	.0420		
		.0400	.0400	.0400	.0420	.0400		
	(AA)	.0397	.0403	.0405	.0404	.0392	.0398	.0005
		.0396	.0400	.0394	.0398	.0392		
	(AA)	.0290	.0293	.0370	.0370	.0352	.0336	.0035
		.0358	.0286	.0295	.0340	.0370		
		.0347	.0362					
	(AA)	.0319	.0324	.0324	.0325	.0323	.0321	.0004
		.0324	.0317	.0321	.0315	.0318		
	(ES)*	.0470	.0500	.0440	.0480	.0550	.0488	.0041
	(AA)	.0450	.0400	.0400	.0450	.0400	.0419	.0023
		.0400	.0450	.0425	.0400	.0440		
		.0410	.0400					
LAB- 1	(NAA)	0.0406	0.0416	0.0412	0.0407	0.0399	.0408	.0006
LAB- 2	(AA)	0.0403	0.0403	0.0407	0.0406	0.0402	.0404	.0002
LAB- 3	(AA)*	0.0272	0.0273	0.0275	0.0278	0.0269	.0273	.0003
LAB- 4	(AA)	0.038	0.038	0.038	0.038	0.038	.0380	.0000
LAB- 5	(AA)	0.039	0.039	0.039	0.039	0.039	.0390	.0000
LAB- 6	(AA)	0.041	0.041	0.042	0.042	0.041	.0414	.0005
LAB- 7	(AA)	0.0322	0.0314	0.0315	0.0313	0.0311	.0315	.0004
LAB- 8	(AA)	0.0389	0.0396	0.0397	0.0416	0.0399	.0399	.0010
LAB- 9	(AA)	0.0402	0.0408	0.0402	0.0398	0.0400	.0402	.0004
LAB-10	(AA)	0.0405	0.0405	0.0380	0.0405	0.0405	.0400	.0011

*Outlying set.

Table 3e - Analytical results, laboratory means and standard deviations for tin in CPB-1

TIN WT %

							MEAN	S.D.
	(COLOR)	.0208	.0164	.0202	.0194	.0188	.0190	.0013
		.0193	.0201	.0191	.0181	.0182		
	(ES)*	.0380	.0400	.0430	.0440	.0420	.0412	.0023
		.0370	.0420	.0430	.0410	.0420		
	(ES)	.0190	.0190	.0190	.0190		.0190	.0000
	(AA)	.0200	.0200	.0250	.0200	.0250	.0213	.0022
		.0200	.0200	.0200	.0200	.0200		
		.0200	.0250	.0250	.0250	.0200		
		.0200	.0200	.0200	.0200	.0200		
	(AA)	.0153	.0161	.0163	.0161	.0160	.0162	.0008
		.0181	.0161	.0157	.0165	.0154		
	(ES)	.0300	.0260	.0310	.0270	.0280	.0284	.0021
	(ES)	.0300	.0320	.0300	.0300	.0280	.0305	.0018
		.0330	.0330	.0300	.0310	.0280		
LAB- 2	(AA)	0.0235	0.0230	0.0234	0.0231	0.0231	.0232	.0002
LAB- 3	(AA)	0.0186	0.0193	0.0193	0.0186	0.0193	.0190	.0004
LAB- 4	(XRF)	0.0063	0.0059	0.0061	0.0065	0.0064	.0062	.0002
LAB- 5	(AA)	0.0130	0.0130	0.0136	0.0118	0.0148	.0132	.0011
LAB- 6	(AA)	0.021	0.021	0.021	0.021	0.021	.0210	.0000
LAB- 7	(XRF)	0.0270	0.0277	0.0265	0.0269	0.0270	.0270	.0004
LAB- 8	(AA)	0.0036	0.0040	0.0044	0.0032	0.0040	.0038	.0005

*Outlying set.

Table 3f - Analytical results, laboratory means and standard deviations for selenium in CPB-1

SELENIUM UG/G

							MEAN	S.D.
	(COLOR)	29.8000	30.0000	30.8000	31.2000	32.0000	30.5500	1.1674
		32.5000	29.7000	30.7000	30.3000	28.5000		
	(COLOR)	32.6000	31.8000	32.2000	32.8000	32.4000	32.4800	.3676
		32.8000	32.2000	32.2000	32.8000	32.8000		
	(COLOR)	27.0000	24.0000	27.0000	25.0000	22.0000	25.4000	1.7127
		27.0000	24.0000	27.0000	25.0000	26.0000		
	(AA)	35.0000	34.0000	33.0000	33.0000	32.0000	33.5000	1.0488
		34.0000						
	(COLOR)	35.0000	36.0000	36.0000	37.0000	36.0000	36.0000	.6667
		36.0000	37.0000	36.0000	35.0000	36.0000		
	(AA)	31.0000	35.0000	29.0000	29.0000	29.0000	32.1000	3.1073
		35.0000	32.0000	36.0000	29.0000	36.0000		
	(AA)	30.0000	29.9000	28.8000	29.1000	29.3000	29.3100	.9259
		28.6000	29.7000	28.8000	29.9000	29.0000		
LAB- 1	(NAA)	33.	34.	35.	32.	35.	33.8000	1.3038
LAB- 2	(COLOR)	26.	26.	26.	26.	26.	26.0000	0.0000
LAB- 3	(AA)	19.	18.	18.	18.	17.	18.0000	.7071
LAB- 4	(COLOR)	24.	26.	26.	26.	26.	25.6000	.8944
LAB- 6	(AA)	32.	32.	33.	32.	32.	32.2000	.4472
LAB- 7	(COLOR)	26.	23.	24.	25.	32.	26.0000	3.9355
LAB- 8	(ICP)	30.	30.	30.	30.	30.	30.0000	0.0000
LAB- 9	(COLOR)*	56.	60.	64.	55.	52.	57.4000	4.6690
LAB-10	(AA)	44.1	39.1	39.1	37.8	36.5	39.3200	3.0813

*Outlying set.

Table 3g - Analytical results, laboratory means and standard deviations for iron in CCU-1

IRON WT %

							MEAN	S.D.
	(TITR)	30.9419	30.9920	30.8918	30.9920	30.7816	30.9235	.0790
		30.9419						
	(TITR)	30.9920	30.8918	30.7916	30.9419		30.9043	.0856
	(TITR)	30.8918	30.8917	30.8717	30.8016	30.8116	30.8136	.0448
		30.8116	30.7916	30.7816	30.7615	30.7615		
	(TITR)	30.6000	30.6000	30.6200	30.6100	30.6000	30.6010	.0160
		30.6000	30.6100	30.5600	30.6100	30.6000		
	(TITR)	31.3600	31.2200	31.2900	31.4500	31.4500	31.3540	.1006
	(TITR)	30.8700	30.9400	30.9400	30.8700	30.9300	30.8300	.1713
LAB- 1	(NAA)	33.3	32.4	32.4	32.6	32.8	32.7000	.3742
LAB- 2	(TITR)	30.63	30.63	30.75	30.82	30.78	30.7220	.0876
LAB- 3	(TITR)	30.59	30.52	30.73	30.60	30.73	30.6340	.0929
LAB- 4	(TITR)	31.04	31.00	30.97	30.99	31.01	31.0020	.0359
LAB- 5	(TITR)	30.93	30.93	30.93	30.98	30.98	30.9500	.0274
LAB- 6	(XRF)	31.64	31.58	31.58	31.55	31.61	31.5920	.0342
LAB- 7	(AA)	29.35	29.38	29.14	29.11	29.46	29.2880	.1545
LAB- 8	(AA)*	35.23	34.88	34.88	34.87	35.01	34.9740	.1544
LAB- 9	(TITR)	30.50	30.24	29.95	30.00	30.00	30.1380	.2818
LAB-10	(AA)*	25.6	26.0	26.0	26.0	26.0	25.9200	.1789

*Outlying set.

Table 3h - Analytical results, laboratory means and standard deviations for sulphur in CCU-1

SULPHUR WT %

							MEAN	S.D.
	(COMB)	36.9000	36.7000	36.6000	36.7500	36.8000	36.8500	.1886
		36.7000	36.9500	37.2000	37.1000	36.8000		
	(GRAV)	35.6313	35.6513	35.6513	35.5711	35.5812	35.6623	.0667
		35.7114	35.7715	35.6112	35.7214	35.7214		
	(GRAV)	35.7000	35.6300	35.7200	35.6100	35.6100	35.6790	.0472
		35.6600	35.7200	35.7000	35.7300	35.7100		
	(GRAV)	35.1200	35.9000	35.4000	35.5600	35.6000	35.5160	.2858
	(GRAV)	35.5500	34.6400	35.5000	35.1900	35.7300	35.3220	.4280
LAB- 1	(PGAA)	34.5	34.3	34.4	35.0	33.6	34.3600	.5030
LAB- 2	(COMB)	35.7	35.8	35.4	35.6	35.7	35.6400	.1517
LAB- 3	(GRAV)	36.26	36.10	36.19	36.32	36.41	36.2560	.1189
LAB- 4	(GRAV)	36.37	36.13	36.31	36.43	36.39	36.3260	.1178
LAB- 5	(GRAV)	36.07	35.72	35.65	35.74	35.84	35.8040	.1635
LAB- 5	(GRAV)	35.19	35.08	35.07	35.18	35.54	35.2120	.1915
LAB- 6	(GRAV)	34.0	33.6	33.9	33.9	34.0	33.8800	.1643
LAB- 7	(GRAV)	35.64	35.67	35.51	35.49	35.70	35.6020	.0958
LAB- 8	(GRAV)	35.78	35.53	35.79	35.58	35.76	35.6880	.1232
LAB- 9	(COMB)	33.26	33.64	33.80	33.52	33.49	33.5420	.1993
LAB-10	*	40.2	39.5	39.6	40.2	39.5	39.8000	.3674

*Outlying set.

Table 3i - Analytical results, laboratory means and standard deviations for arsenic in CCU-1

ARSENIC UG/G

							MEAN	S.D.
	(COLOR)	44.0000	44.2000	41.8000	40.2000	43.8000	44.3400	2.0828
		45.6000	44.8000	46.2000	45.6000	47.2000		
	(COLOR)	41.0000	50.0000	47.0000	46.0000	49.0000	51.8000	7.3756
		61.0000	60.0000	63.0000	54.0000	47.0000		
	(COLOR)	35.0000	34.0000	33.0000	32.0000	33.0000	33.5000	1.9570
		31.0000	32.0000	32.0000	37.0000	36.0000		
	(COLOR)	54.0000	54.0000	52.0000	54.0000	54.0000	55.0000	3.0185
		62.0000	52.0000	56.0000	58.0000	54.0000		
	(COLOR)	42.0000	42.0000	51.0000	48.0000	47.0000	46.0833	3.4234
		48.0000	50.0000	42.0000	48.0000	47.0000		
		41.0000	47.0000					
	(COLOR)	40.0000	30.0000	40.0000	40.0000	30.0000	35.5556	5.2705
		30.0000	40.0000	30.0000	40.0000			
	(NAA)	43.6000	42.2000	43.9000	43.9000	44.3000	44.7833	2.0980
		50.4000	45.2000	46.2000	44.7000	42.9000		
		45.8000	44.3000					
	(COLOR)	48.0962	46.0922	48.0962	48.0962	48.0962	46.9940	2.8517
		39.0782	48.0962	48.0962	48.0962	48.0962		
	(COLOR)	28.8000	31.3000	31.6000	30.0000	31.4000	30.8000	1.0635
		31.0000	32.3000	31.6000	30.2000	29.8000		
	(ES)*	70.0000	55.0000	60.0000	100.0000	75.0000	72.0000	17.5357
	(AA)	24.3000	22.1000	28.7000	23.2000	29.8000	25.4000	3.1113
		28.7000	23.2000	23.2000				
LAB- 1	(NAA)	51.	49.	51.	50.	48.	49.8000	1.3038
LAB- 2	(COLOR)	41.7	41.0	41.5	42.1	41.6	41.5800	.3962
LAB- 3	(COLOR)	36.	39.	38.	40.	38.	38.2000	1.4832
LAB- 4	(TITR)	38.	38.	38.	37.	37.	37.6000	.5477
LAB- 5	(COLOR)	40.	40.	40.	40.	40.	40.0000	0.0000
LAB- 6	(NAA)	49.	51.	50.	51.	53.	50.8000	1.4832
LAB- 7	(COLOR)	35.	32.	39.	34.	36.	35.2000	2.5884
LAB- 8	(AA)	32.	44.	58.	40.	42.	43.2000	9.4446
LAB- 9	(COLOR)	48.	40.	42.	50.	43.	44.6000	4.2190
LAB-10	(AA)	35.	35.	32.	38.	36.	35.2000	2.1679
LAB-10	(AA)	33.	32.	29.	30.	29.	30.6000	1.8166

*Outlying set.

Table 3j - Analytical results, laboratory means and standard deviations for selenium in CCU-1

SELENIUM UG/G

							MEAN	S.D.
	(COLOR)	105.0000	100.0000	111.0000	104.0000	104.0000	104.6000	3.6878
		98.0000	106.0000	104.0000	106.0000	108.0000		
	(COLOR)	103.0000	105.0000	110.0000	107.0000	100.0000	105.7000	6.3605
		96.0000	110.0000	110.0000	117.0000	99.0000		
	(XRF)	127.0000	124.0000	136.0000	129.0000	130.0000	127.5000	3.5355
		124.0000	126.0000	126.0000	126.0000	127.0000		
	(COLOR)	140.0000	120.0000	130.0000	130.0000	120.0000	123.0000	9.4868
		110.0000	110.0000	120.0000	120.0000	130.0000		
	(COLOR)	129.0000	126.0000	126.0000	131.0000	127.0000	128.0000	2.2608
		131.0000	131.0000	127.0000	126.0000	126.0000		
	(XRF)	60.0000	70.0000	60.0000	60.0000	70.0000	65.0000	5.2705
		70.0000	60.0000	70.0000	60.0000	70.0000		
	(AA)	139.0000	140.0000	154.0000	147.0000	144.0000	142.5000	6.6542
		136.0000	133.0000	150.0000	145.0000	137.0000		
	(AA)	117.5000	114.8000	114.3000	113.0000	114.6000	114.6600	1.5094
		117.1000	114.5000	113.6000	113.9000	113.3000		
	(AA)	116.7000	116.7000	129.2000	125.0000	129.2000	124.2500	5.6702
		120.9000	125.0000	131.3000				
LAB- 1	(NAA)	132.	128.	129.	130.	131.	130.0000	1.5811
LAB- 2	(COLOR)	117.	116.	115.	122.	118.	117.6000	2.7019
LAB- 3	(AA)*	66.	68.	64.	63.	64.	65.0000	2.0000
LAB- 4	(COLOR)	125.	125.	125.	125.	125.	125.0000	0.0000
LAB- 6	(AA)	130.	130.	138.	144.	140.	136.4000	6.2290
LAB- 7	(COLOR)	72.	86.	72.	65.	64.	71.8000	8.7864
LAB- 8	(XRF)	120.	120.	130.	120.	110.	120.0000	7.0711
LAB- 9	(COLOR)	115.	128.	119.	130.	129.	124.2000	6.7602

*Outlying set.

Table 3k - Analytical results, laboratory means and standard deviations for tungsten in MP-1a

TUNGSTEN WT %

							MEAN	S.D.
	(NAA)	.0470	.0440	.0490	.0460	.0490	.0470	.0021
	(XRF)	.0477	.0446	.0481	.0459	.0482	.0459	.0021
	(ES)	.0290	.0294	.0298	.0294	.0296	.0294	.0003
	(COLOR)	.0440	.0400	.0400	.0400	.0440	.0416	.0022
	(AA)	.0360	.0360	.0410	.0380	.0400	.0382	.0023
	(COLOR)	.0530	.0490	.0480	.0470	.0490	.0492	.0023
	(COLOR)	.0380	.0410	.0380	.0360	.0360	.0378	.0020
	(COLOR)	.0350	.0360	.0360	.0370	.0380	.0364	.0011
	(COLOR)	.0450	.0450	.0400	.0470	.0470	.0448	.0029
	(COLOR)	.0350	.0320	.0320	.0290	.0350	.0326	.0025
	(COLOR)	.0436	.0467	.0422	.0417	.0456	.0440	.0022
	(COLOR)	.0310	.0320	.0320	.0320	.0330	.0320	.0007
LAB- 1	(NAA)	0.0460	0.0485	0.0475	0.0474	0.0482	.0475	.0010
LAB- 2	(XRF)	0.043	0.046	0.046	0.037	0.044	.0432	.0037
LAB- 3	(COLOR)	0.026	0.024	0.025	0.029	0.026	.0260	.0019
LAB- 4	(COLOR)	0.046	0.047	0.047	0.046	0.046	.0464	.0005
LAB- 5	(COLOR)*	0.066	0.075	0.063	0.059	0.059	.0644	.0066
LAB- 6	(NAA)	0.0458	0.0454	0.0448	0.0447	0.0447	.0450	.0006
LAB- 7	(XRF)	0.060	0.058	0.058	0.062	0.062	.0600	.0020
LAB- 8	(XRF)	0.020	0.020	0.020	0.019	0.021	.0200	.0007
LAB-10	(COLOR)	0.0240	0.0240	0.0240	0.0240	0.0240	.0240	0.0000

*Outlying set.

Table 3a - Analytical results, laboratory means and standard deviations for tin in MP-2

TIN WT %

							MEAN	S.D.
	(AA)	.0440	.0390	.0410	.0390	.0390	.0404	.0022
	(AA)	.0440	.0470	.0540	.0480	.0510	.0488	.0038
	(XRF)	.0430	.0440	.0440	.0420	.0430	.0434	.0011
	(XRF)	.0400	.0420	.0400	.0390	.0400	.0402	.0011
	(XRF)*	.1200	.1300	.1200	.1100	.1200	.1200	.0071
	(AA)	.0389	.0377	.0372	.0372	.0383	.0379	.0007
	(AA)	.0500	.0480	.0490	.0500	.0470	.0488	.0013
LAB- 2	(XRF)	0.047	0.048	0.047	0.046	0.045	.0464	.0011
LAB- 3	(AA)	0.0386	0.0379	0.0372	0.0372	0.0381	.0378	.0006
LAB- 4	(XRF)	0.044	0.046	0.045	0.046	0.047	.0456	.0011
LAB- 5	(AA)	0.040	0.039	0.034	0.032	0.029	.0348	.0047
LAB- 6	(XRF)	0.039	0.036	0.036	0.036	0.038	.0370	.0014
LAB- 7	(XRF)	0.047	0.048	0.047	0.048	0.048	.0476	.0005
LAB- 8	(AA)	0.042	0.045	0.045	0.045	0.045	.0444	.0013

*Outlying set.

DISCUSSION

Table 4 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separation and determination steps. No attempt was made to detect if there is a statistically significant difference between the overall means of the more popular methods.

The histograms of the analytical results for the various elements are shown in Fig. 1 and with the exception of bismuth in CZN-1 illustrate a good degree of consensus between participating laboratories. This fact is also demonstrated in Table 4 wherein the mean of all accepted results, as given by

$$\bar{\bar{x}} = \sum_{i}^{k} \sum_{j}^{n_i} x_{ij} \Big/ \sum_{j=1}^{k} n_i$$

and the median value are compared. A significant difference in value is noted only for bismuth. An examination of Table 3a for bismuth points out there is a preponderance of results whose mean value lies below 40 µg/g; 17 out of 24 sets, excluding the obvious outlier at $\bar{x}_i$ = 601.2 µg/g.

The overall mean value (i.e., mean of individual laboratory means) of these 17 sets is 27.4 µg/g, which is in excellent accord with the median found for all accepted results. The authors conclude therefore that a value of 27 µg/g is a better estimate of the bismuth content of CZN-1 than the overall mean value of all accepted results, i.e., $\bar{\bar{x}}$.. = 39 µg/g and propose a recommended value of 27 µg/g for bismuth in CZN-1.

No attempt was made to assess the combined results of the initial and current interlaboratory programs according to the criteria for certification employed by CCRMP (9). It was considered unwarranted to do so because of differences in the organization of the two programs.

Table 4 - Overall mean and median values

Reference material	Element	Overall mean	Median
CZN-1	Bi	38 µg/g	27 µg/g
	Sn	70 µg/g	71 µg/g
	Se	5.3 µg/g	5.0 µg/g
CPB-1	Mn	0.039%	0.040%
	Sn	0.020%	0.020%
	Se	30.3 µg/g	30.5 µg/g
CCU-1	Fe	30.85%	30.84%
	S	35.5%	35.7%
	As	41 µg/g	42 µg/g
	Se	120 µg/g	124 µg/g
MP-1a	W	0.040%	0.041%
MP-2	Sn	0.043%	0.043%

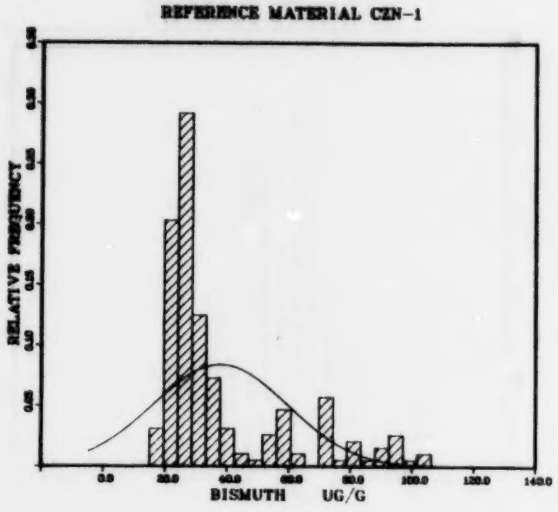

Figure 1a - Histogram for bismuth in CZN-1

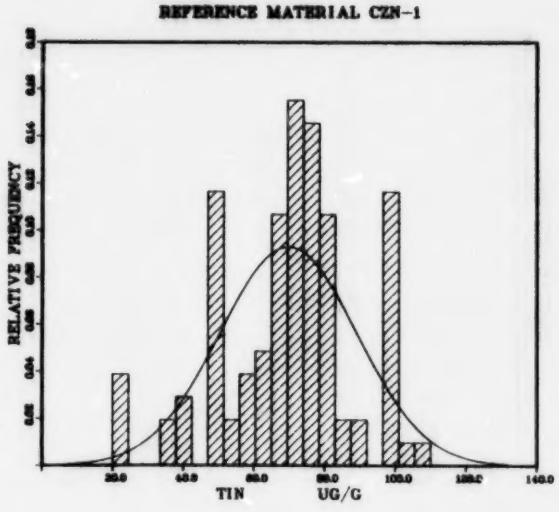

Figure 1b - Histogram for tin in CZN-1

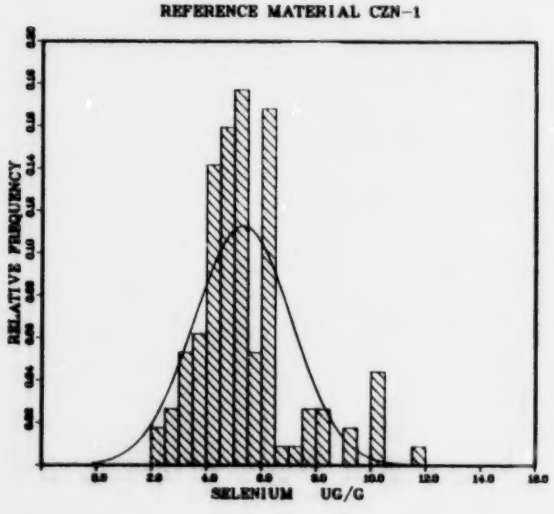

Figure 1c - Histogram for selenium in CZN-1

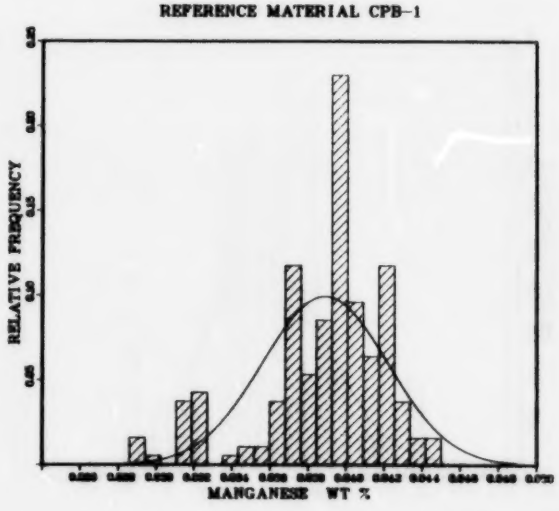

Figure 1d - Histogram for manganese in CPB-1

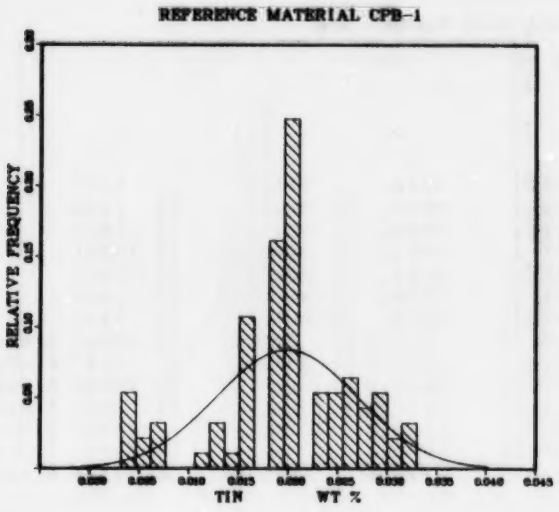

Figure 1e - Histogram for tin in CPB-1

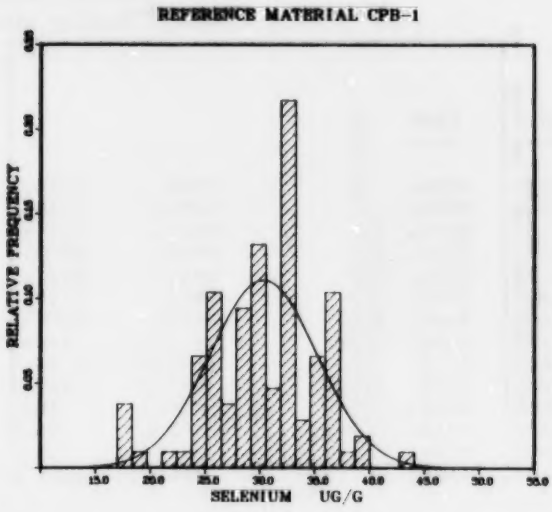

Figure 1f - Histogram for selenium in CPB-1

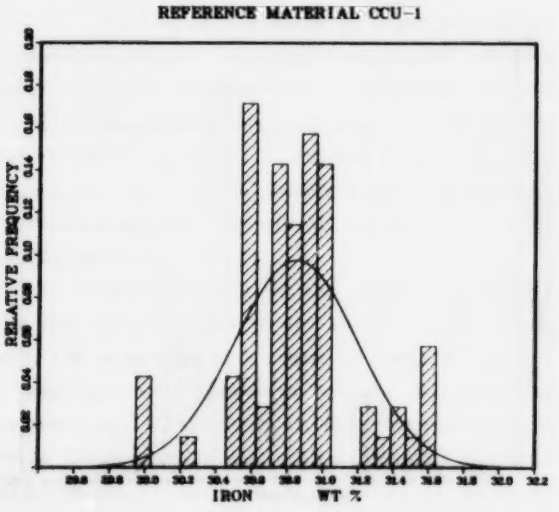

Figure 1g - Histogram for iron in CCU-1

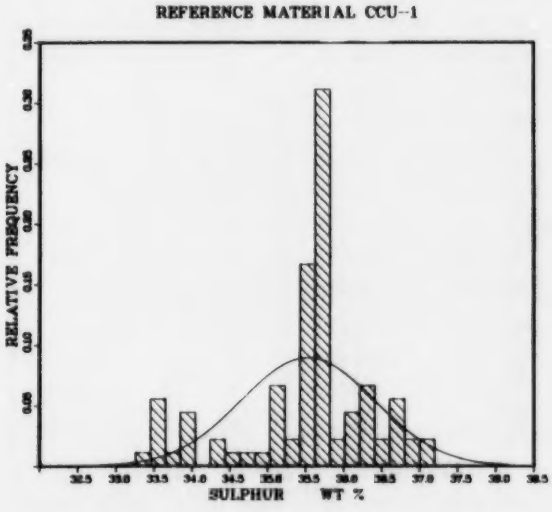

Figure 1h - Histogram for sulphur in CCU-1

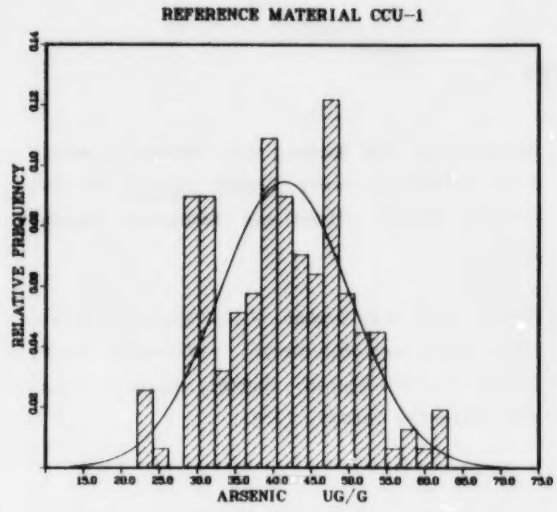

Figure 1i - Histogram for arsenic in CCU-1

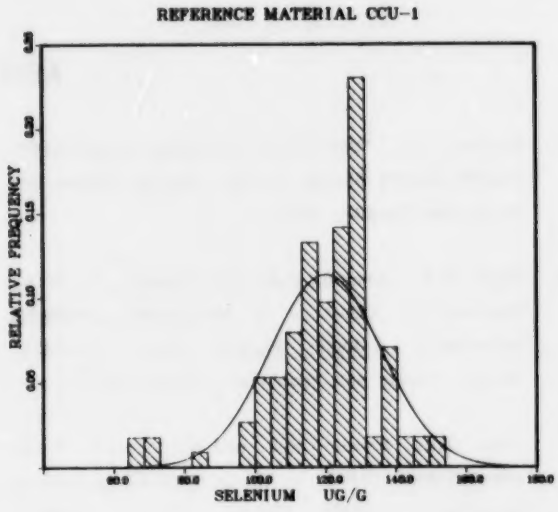

Figure 1j - Histogram for selenium in CCU-1

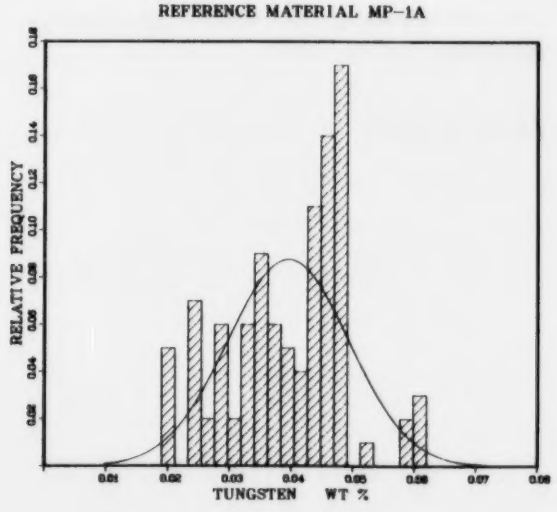

Figure 1k - Histogram for tungsten in MP-1a

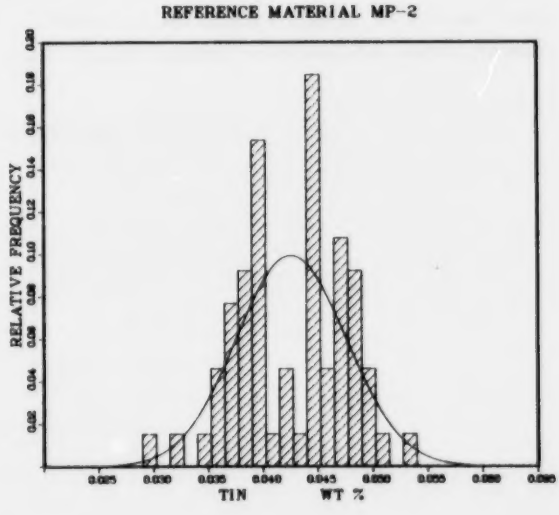

Figure 1l - Histogram for tin in MP-2

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1. Steger, H.F. "Certified reference materials"; CANMET Report 83-3E; CANMET, Energy, Mines and Resources Canada; 1983.

2. Faye, G.H., Bowman, W.S. and Sutarno, R. "Zinc concentrate CZN-1 - A certified reference material"; CANMET Report 79-14; CANMET, Energy, Mines and Resources Canada; 1979.

3. Faye, G.H., Bowman, W.S. and Sutarno, R. "Lead concentrate CPB-1 - A certified reference material"; CANMET Report 79-15; CANMET, Energy, Mines and Resources Canada; 1979.

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5. Steger, H.F. and Bowman, W.S. "MP-1a: A certified reference ore"; CANMET Report 82-14E; CANMET, Energy, Mines and Resources Canada; 1982.

6. Steger, H.F. and Bowman, W.S. "MP-2 - A certified tungsten-molybdenum reference ore"; CANMET Report 83-14E; CANMET, Energy, Mines and Resources Canada; 1983.

7. Brownlee, K.A. "Statistical theory and methodology in science and engineering"; John Wiley and Sons, Inc., New York; 1960.

8. Steger, H.F. "A re-assessment of the criteria for certifiability in CCRMP"; Geostandards Newsletter 6:17-23; 1982.

APPENDIX A

PARTICIPATING LABORATORIES

Participating Laboratories

CANMET Contract	Laboratory
035Q.23440-3-9164-1	Neutron Activation Services Hamilton, Ontario
035Q.23440-3-9164-2	Lakefield Research of Canada Ltd. Lakefield, Ontario
035Q.23440-3-9164-3	Kamloops Research and Assay Laboratory Kamloops, British Columbia
035Q.23440-3-9164-4	Bondar-Clegg and Company Ltd. Ottawa, Ontario
035Q.23440-3-9164-5	Bondar-Clegg and Company Ltd. North Vancouver, British Columbia
035Q.23440-3-9164-6	X-Ray Assay Laboratories Ltd. Don Mills, Ontario
035Q.23440-3-9164-7	Atlantic Analytical Services Ltd. Saint John, New Brunswick
035Q.23440-3-9164-8	Materials Research Laboratory Nepean, Ontario
035Q.23440-3-9164-9	Technical Services Laboratories Mississauga, Ontario
035Q.23440-3-9164-10	Barringer Magenta Ltd. Rexdale, Ontario